

1111165

# PATENT SPECIFICATION

NO DRAWINGS

1111.165

Date of Application and filing Complete Specification: 4 April, 1966.

No. 14780/66.

Application made in United States of America (No. 445,796) on 5 April, 1965.

Complete Specification Published: 24 April, 1968.

© Crown Copyright 1968.



Index at acceptance:—D2 B(14F, 14H, 14X)

Int. Cl.:—D 21 h 3/02

## COMPLETE SPECIFICATION

### Fibrous Web having improved Wet Strength and method of its manufacture

We, THE DEXTER CORPORATION formerly C. H. Dexter & Sons Incorporated, a Corporation organised and existing under the Laws of the State of Connecticut, United States of America, of Windsor Locks, Connecticut, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a fibrous web material exhibiting improved wet strength and to the method of its manufacture.

In recent years increased emphasis has been placed upon the use of wet-strength resins which are operable in the alkaline or neutral pH range. Such resins, commonly referred to as "alkaline-curing" resins, are particularly desirable since they permit machine operation under the less corrosive, nonacid conditions while at the same time imparting improved strength and softness to the paper and permitting the use of alkaline fillers. The introduction of these alkaline curing wet strength resins to the industry has met with varying degrees of success. Predominant among those presently in use are the water-soluble cationic resins falling under the general category of epoxidized polyamides. The epoxidized materials broadly consist of polymeric reaction products of epichlorohydrin and a polyamide. These resins are generally thermo-setting materials which may be utilized under alkaline conditions, applied to the fibers in dilute aqueous suspensions and finally cured to a water-insoluble state. The resins have also been employed in conjunction with relatively small amounts of certain water-soluble gums to advantageously improve the wet strength of paper products. However, when employed in conjunction with such gums and when used as a post-formation treatment of the paper, it has been found that the papers tended to lose a substantial degree

[Price 4s. 6d.]

of their wet strength at high humidity conditions.

Accordingly it is an object of the present invention to improve the wet strength of papers treated with alkaline-curing resins and particularly to impart thereto the ability to retain their wet strength at high humidity for prolonged periods of time.

Another object of the present invention is to provide a new and improved process for imparting to a paper treated with an alkaline-curing resin an unexpected increase in the wet strength thereof in a relatively simple, rapid, facile, and economical manner.

A further object of the present invention is to provide a paper exhibiting not only improved initial and prolonged wet strength and retained wet strength at high humidity but also a paper which exhibits the characteristics of acid curing treatments while at the same time retaining the desirable characteristics of alkaline curing wet strength resins.

According to this invention there is provided a method of improving the wet strength of fibrous web materials while preventing degradation of the dry strength thereof comprising the steps of treating a preformed fibrous web material with an aqueous alkaline solution comprising a water-soluble gum in the form of carboxymethyl cellulose and a water soluble alkaline-curing resin, said solution being maintained with a pH above 9; drying and acidifying the alkaline treated web with acid solution to produce a fibrous web material having enhanced wet strength, and a paper pH within the range of 3 to 6 as determined by TAPPI test method T435—m—52.

In carrying out the process of the present invention a fibrous paper is initially produced in the form of a continuous web material in accordance with known and conventional paper-making techniques. The paper web material is subjected to a post-formation wet strengthening treatment with an alkaline solu-

tion of an alkaline-curing cationic resin and a water-soluble gum following which preferably the resin-coated paper is dried and the pH of the resultant web is lowered to 6.0 to 3 prior to final washing, pressing, and drying operations.

The cationic resin and the gum are generally mixed prior to their application to the preformed fibrous web. The mixture takes the form of a aqueous solution having an alkaline pH and may be prepared by dissolving the resin and water-soluble gum in an alkaline solution, such as a dilute sodium hydroxide solution, and then adjusting both the concentration of the components and pH of the solution to attain the desired results. The pH of the solution is maintained above 9.0, with the preferred operating pH being 10 to 11. As shown in Example Six herein, papers treated with a resin/gum solution having a pH on the acid side exhibit a degradation in strength when further treated in accordance with the present invention.

The concentration of the components in the alkaline solution will vary somewhat depending on the particular web being treated as well as on the particular alkaline-curing resin and water-soluble gum employed. In general it has been found that satisfactory results can be achieved at various gum to resin ratios, however, in practice this ratio is usually maintained at greater than 1:1, ratios of 2:1 to 15:1 giving excellent results. The concentration of the water-soluble gum in the alkaline solution may vary from about 0.1 per cent by weight up to about 10.0 per cent by weight. However, the preferred concentration is from 0.5 to 5.0 per cent by weight and, more specifically, 1.0 to 2.0 per cent. Amounts in excess of 10.0 per cent are generally not employed since the increased amount does not result in a proportional increase in the strength of the web treated thereby. The alkaline-curing resin may be effectively used in concentrations up to 5.0 per cent by weight or more. Generally an operating range from about 0.01 to 1.0 per cent has been found suitable with the preferred range being 0.05 to 0.5 per cent by weight.

The cationic alkaline-curing resins suitable for use in accordance with the present invention are preferably the uncured thermosetting epoxidized polyamide resins, exemplary of which are the resins described in United States Patent Nos. 2,926,116 and 3,125,552. The resins are water-soluble polymeric reaction products of epichlorohydrin and polyamides containing secondary amine groups. The epichlorohydrin acts in a manner similar to cross-linking agent by reacting with secondary amine groups within the polyamides resulting in a conversion of the secondary amines to tertiary amines, the vicinal epoxy ring being available for the cross-linking process. Generally, polyamides derived from polyalkylene polyamines and saturated or un-

saturated aliphatic or aromatic polycarboxylic acids containing from 3 to 10 carbon atoms are preferred. A typical example of such material is the water-soluble epichlorohydrin-polyamide reaction product sold by Hercules Powder Company, Wilmington, Delaware, under the name "Kymene 557." (Registered Trade Mark).

The water-soluble gum used is one of the various types of sodium carboxymethyl-cellulose (CMC), sometimes referred to as sodium cellulose glycolate.

The paper or fibrous sheet material is generally formed in the usual papermaking fashion in the form of long, continuous webs which can be easily rolled up on collecting spools. These preformed fibrous webs, after partial or complete drying, are treated with the alkaline solution in accordance with conventional solution treatment techniques such as by tub application. In this regard excellent results have been obtained utilizing an immersion or dip-coating process to obtain the desired impregnation of the web. The coated or impregnated web is then dried and, in accordance with the present invention, subjected to an acid treating step which imparts to the sheet material the desired improvement in wet strength while lowering the paper pH to 6.0 to 3.0.

The acid bath or treatment is generally applied by tub application although most coating techniques may be employed with good results. The bath generally consists of a dilute solution of an inorganic or organic acid or acid salt having a concentration of 5.0 per cent by weight or less. The acids utilized may be the common mineral or inorganic acids such as hydrochloric or sulfuric acid; the organic acids such as acetic, fumaric or lactic acid; or the acid producing salts such as aluminum sulfate, and ammonium chloride. The preferred acid solutions are generally of a concentration greater than 0.01 and less than about 1.0 per cent by weight, the exact utilizable range varying with the type of acid employed. It will of course be appreciated that acid concentrations higher than those set forth herein may be utilized where the web is subsequently washed for an extended period of time. For example, the strong mineral acids, such as sulfuric acid, may be utilized at concentrations greater than 0.5 per cent and yield excellent results where the paper pH is about 5.0, see Example Two, while at concentrations of less than 0.20 per cent by weight yield poor results where the paper pH is about 3.5, as evidenced by Example Seven.

The acid treatment markedly increases the acidity of the ultimate product and preferably results in a paper web material whose extract possesses a pH of 6.0 or less. However, when the pH of mineral acid treated papers drops below about 3.5 the acidity of the web causes degradation in the strength and structural

integrity of the web, it being understood, of course, that organic acid treated papers may exhibit a lower pH and still retain their high strength characteristics due to their weaker activity.

After the acid treatment the web is generally washed with water for a brief interval prior to drying and collection in the conventional manner. The principal purpose of the washing operation is to remove the excess nonsubstantive materials and particularly the excess acid from the web before it passes through the heated driers. The washing time is generally kept to a minimum, however, so as not to completely leach out the acid applied to the web.

The term "ream weight" as used herein refers to the weight in pounds of 480 sheets each being 24 inches wide and 36 inches long, in accordance with TAPPI test method T410—os—61 or its related standard.

The term "paper pH" as used herein refers to the pH as determined by TAPPI test method T435—m—52 for "Hydrogen Ion Concentration of Paper Extracts" in accordance with the cold extraction procedure. That procedure consists of placing 1.0 gram of air dry paper in a 100 ml. beaker to which is added 20 ml. of distilled water. The paper is macerated with a glass rod until uniformly wet after which an additional 50 ml. of water is added to the beaker. The beaker is then covered and allowed to stand for one hour. At the end of this time the solution is stirred and the pH of the unfiltered mixture is measured at room temperature.

The wet tensile strength values set forth herein have been obtained according to TAPPI test method T456—m—49. This method requires that the paper being tested be completely saturated with water at room temperature prior to measuring the tensile strength according to TAPPI test method T404—os—61.

Having generally described the invention, the following examples are included for purposes of illustration so that the invention may be more readily understood and are in no way intended to limit the scope of the

invention unless otherwise specifically indicated. All amounts are on a weight basis unless otherwise specified.

#### EXAMPLE ONE

A preformed fibrous sheet having a ream weight of 14.5 pounds and comprising 100 per cent hemp fibers was dip-coated with an aqueous alkaline solution having a pH of 10.0, a sodium carboxymethylcellulose (CMC) concentration of 1.0 per cent by weight and about 0.1 per cent by weight of a polymeric reaction product of epichlorohydrin and a polyamide ("Kymene 557"). The sheet was then dried. A first portion of the treated sheet, designated 1—A, was simply washed with water and dried. A second portion of the treated sheet, designated 1—B, was dipped in a 1.0 per cent hydrochloric acid solution, washed with water, pressed, and dried.

Both sheets were subsequently tested for wet tensile strength and paper pH in accordance with standard TAPPI test methods. Sheet 1—A had a paper pH of 6.2 and a wet tensile strength of 922 grams per inch width while the acid treated portion, sheet 1—b, had a paper extract pH value of 5.6 and a wet strength of 1040. After permitting both sheets to age for 23 months at room temperature, the wet strength of sheet 1—A had dropped to 842 grams per inch width while the wet strength of the acid treated paper had increased to 1500 grams per inch width. Thus the tests indicated not only a higher initial wet strength for the acid treated paper but also a substantial increase in the wet strength of the paper upon aging.

#### EXAMPLE TWO

A 7.25 pound ream weight paper was produced from a furnish containing about 1/3 wood and 2/3 hemp fibers and a minor amount, less than 1.0 per cent by weight, of an epoxidized polyamide ("Kymene 557") and karaya gum. Following the procedure of Example One, test samples of the paper were all dip-coated in dilute aqueous solutions, treated with the acid solutions as indicated in Table I and tested. Particularly significant are the wet tensile strengths before and after storage at high humidity.

TABLE I

Examples	2—A	2—B	2—C	2—D
<u>Resin/CMC Treatment</u>				
Resin Conc.	0.17%	0.17%	0.19%	0.19%
CMC Conc.	1.58%	1.58%	1.88%	1.88%
Solution pH	10.0	10.0	10.0	10.0
<u>Acid Treatment</u>				
Type	—	H <sub>2</sub> SO <sub>4</sub>	—	H <sub>2</sub> SO <sub>4</sub>
Conc.	—	0.58%	—	0.77%
Paper pH	7.7	4.1	8.5	4.9
<u>Wet Tensile Strength (gm/in width)</u>				
At time of treatment	400	546	458	528
After ambient cure for about 3 weeks	455	580	—	—
After 3 weeks ambient cure plus 1 week at 95% humidity and 120° F.	120	600	—	—
After ambient cure for 17 months	328	669	—	—
After ambient cure for 21 months	—	—	469	748

## EXAMPLE THREE

A 7.25 pound ream weight paper comprising 1/3 wood and 2/3 hemp fibers and no beater additives was treated with aqueous alkaline solutions containing CMC and an

epoxidized polyamide resin ("Kymene 557") prior to dip-coating in a dilute acid solution. The treatments and results are tabulated in Table II.

TABLE II

Ex.	Resin/CMC Treatment			Acid Treatment		Paper pH	Wet Tensile Strength (gm/in width)			
	Resin Conc.	CMC Conc.	Solution pH	Type	Conc.		At time of treatment	Ambient cure for 2 months	Oven cure*	Humidity test**
3-A	0.09%	1.2%	10.6	—	—	8.4	270	338	—	—
3-B	0.09%	1.2%	10.6	H <sub>2</sub> SO <sub>4</sub>	0.064%	5.3	330	458	—	—
3-C	0.12%	1.2%	10.5	—	—	7.5	215	—	364	—
3-D	0.12%	1.2%	10.5	H <sub>2</sub> SO <sub>4</sub>	0.032%	6.0	256	—	382	—
3-E	0.12%	1.2%	10.5	H <sub>2</sub> SO <sub>4</sub>	0.064%	5.0	433	—	613	—
3-F	0.17%	1.5%	10.5	—	—	7.0	425	—	—	321
3-G	0.17%	1.5%	10.5	H <sub>2</sub> SO <sub>4</sub>	0.032%	5.8	489	—	—	499
3-H	0.17%	1.5%	10.5	H <sub>2</sub> SO <sub>4</sub>	0.16%	5.3	516	—	—	585

\* Cured for 10 min. at 350° F.

\*\* Samples kept at 80% relative humidity and 76° F. for one week.

## EXAMPLE FOUR

5 This example illustrates the improved result obtained from the acid treatment of the present invention when the concentration ratio between the resin and the water-soluble gum is substantially varied.

Separate portions of a 100 per cent hemp fiber web having a ream weight of 12.85 pounds was treated with aqueous alkaline

10 solutions having gum to resin ratios of 5:1 and 15:1. All other factors were kept substantially identical. The alkaline solutions each had a pH of 10.0 and each acid treated sheet was dip-coated in a 0.064% sulfuric acid solution. The concentrations of the alkaline 15 resin solutions are given in Table III along with the test results.

TABLE III

Examples	4—A	4—B	4—C	4—D
<u>Resin/CMC Treatment</u>				
Resin Conc.	0.3%	0.3%	0.1%	0.1%
CMC Conc.	1.5%	1.5%	1.5%	1.5%
Acid Treatment	no	yes	no	yes
<u>Paper pH</u>	7.45	5.55	7.45	5.80
<u>Wet Tensile Strength (gm/in width)</u>				
At time of treatment	732	755	467	572
Oven cure at 350° F. for 10 min.	832	1110	745	881

## EXAMPLE FIVE

20 This example illustrates the effect of low paper pH wherein the gum/resin ratios are 10:1 and 2:1.

25 A hemp fiber web having a ream weight of 12 pounds was dip-coated with an alkaline CMC/epoxidized polyamide ("Kymene 557")

solution, dried, acid treated, and finally dried. The web was not washed with water after the acid treatment. The results as set forth in Table IV indicate that a mineral acid treatment resulting in a paper pH of about 30 3.5 or lower tends to degrade both the dry and wet strength of the web.

TABLE IV

Ex.	Resin/CMC Treatment			Acid Treatment		Paper pH	At time <sup>st</sup> of 350° F. for treatment 10 min.	Dry Tensile Strength (gm/in width)	
	Resin Conc.	CMC Conc.	Solution pH	Type	Conc.				
5-A	0.1%	1.0%	10.2	—	—	6.7	534	731	3244
5-B	0.1%	1.0%	10.2	H <sub>2</sub> SO <sub>4</sub>	0.096%	5.6	582	862	3125
5-C	0.1%	1.0%	10.2	H <sub>2</sub> SO <sub>4</sub>	0.192%	3.5	642	280	1760
5-D	0.5%	1.0%	10.2	—	—	7.3	880	1040	3150
5-E	0.5%	1.0%	10.2	H <sub>2</sub> SO <sub>4</sub>	0.096%	5.5	1010	1235	3540
5-F	0.5%	1.0%	10.2	H <sub>2</sub> SO <sub>4</sub>	0.192%	3.6	910	495	2690

## EXAMPLE SIX

This example illustrates the effect of utilizing an acid solution of gum resin in place of the highly alkaline solution of the present invention.

Paper samples from a hemp fiber web having a ream weight of 12 pounds were treated

with a solution of 1.0 per cent by weight CMC and 0.1 per cent by weight epoxidized polyamide ("Kymene 557") having the indicated solution pH. The test results set forth in Table V indicate the necessity of using an alkaline rather than an acid solution.

TABLE V

Examples	Resin/CMC Solution pH	Acid Treatment		Paper pH	Wet Tensile Strength (gm/in width)		Dry Tensile Strength (gm/in width)
		Type	Conc.		At time of treatment	Oven cure at 350° F. for 10 min.	
6-A	10.2	—	—	6.7	534	731	3244
6-B	10.2	H <sub>2</sub> SO <sub>4</sub>	0.096%	5.6	582	862	3125
6-C	5.9	—	—	6.1	543	745	3309
6-D	5.9	H <sub>2</sub> SO <sub>4</sub>	0.096%	3.4	640	483	648
6-E	4.0	—	—	6.1	486	727	3062
6-F	4.0	H <sub>2</sub> SO <sub>4</sub>	0.096%	3.6	564	374	570
6-G	2.0	—	—	4.6	412	809	2894
6-H	2.0	H <sub>2</sub> SO <sub>4</sub>	0.096%	3.6	552	410	565

## EXAMPLE SEVEN

This example illustrates the beneficial result obtained from using organic as well as inorganic acids.

- 5 A hemp paper web having a ream weight of 12 pounds was treated with an alkaline

solution having a pH of 10.2 and comprising 1.0 per cent by weight CMC and 0.1 per cent by weight epoxidized polyamide ("Kymene 557"). The treated web was dried and samples thereof were acid treated as indicated in Table VI.

TABLE VI

Examples	7—A	7—B	7—C	7—D
<u>Acid Treatment</u>				
Type	—	H <sub>2</sub> SO <sub>4</sub>	acetic	lactic
Conc.	—	0.096%	0.45%	0.45%
Paper pH	6.7	5.6	4.2	3.6
<u>Wet Tensile Strength (gm/in width)</u>				
At time of treatment	534	582	580	638
Oven cure at 350° F. for 10 min.	731	862	970	995
<u>Dry Tensile Strength (gm/in width)</u>				
	3244	3125	3240	2900

## WHAT WE CLAIM IS:—

- 15 1. A method of improving the wet strength of fibrous web materials while preventing degradation of the dry strength thereof comprising the steps of treating a preformed fibrous web material with an aqueous alkaline solution comprising a water-soluble gum in the form of carboxymethyl cellulose and a water soluble alkaline-curing resin, said solution being maintained with a pH above 9; drying and acidifying the alkaline treated web with acid solution to produce a fibrous web material having enhanced wet strength, and a paper pH within the range of 3 to 6 as determined by TAPPI test method T435—m—52.
- 20 2. A method as claimed in claim 1, wherein the water-soluble alkaline-curing resin is a water-soluble reaction product of epichlorohydrin and a polyamide.
- 25 3. A method as claimed in claim 2 wherein the solution comprises 0.01 to 1.0 per cent by weight of the water-soluble reaction product of epichlorohydrin and a polyamide containing secondary amine groups, the ratio of gum to resin being greater than 1:1.
- 30 4. A method as claimed in claim 3, wherein

the solution comprises 1.0 to 2.0 per cent of weight of carboxymethylcellulose and 0.05 to .5 per cent by weight of the water-soluble reaction product, said reaction product having only tertiary amine groups.

5. A method as claimed in any one of the claims 1 to 4, wherein the pH of the solution is between 9 to 11 and the acid concentration is less than 5 per cent by weight.

6. A method as claimed in claim 5, wherein the acid concentration is 0.01 to 1.0 per cent by weight.

7. A fibrous web material treated in accordance with the method of claim 1.

8. A fibrous web material treated in accordance with the method of claim 3.

9. A fibrous web material treated in accordance with the method of claim 4.

10. A fibrous web material treated in accordance with the method of claim 6.

11. A method of improving the wet strength of fibrous web materials as claimed in claim 1 substantially as herein described with reference to the examples.

MARKS & CLERK,  
Chartered Patent Agents.  
Agents for the Applicants.